

BLEACHING COMPOSITION**FIELD OF INVENTION**

This invention relates to the enhancement of bleaching
5 compositions that are substantially devoid of peroxy species.

BACKGROUND OF INVENTION

The use of bleaching catalysts for stain removal has been
10 developed over recent years. The recent discovery that
some catalysts are capable of bleaching effectively in
the absence of an added peroxy source has recently
become the focus of some interest, for example:
WO9965905; WO0012667; WO0012808; WO0029537, and,
15 WO0060045.

The shelf life of a product may be regarded as the period
of time over which the product may be stored whilst
retaining its required quality. A satisfactory shelf
20 life is in many instances a crucial factor for the
success of a commercial product. A product with a short
shelf life generally dictates that the product is made in
small batches and is rapidly sold to the consumer. It is
also a concern to the owners of a brand with a short
25 shelf life that the consumer uses the product within the
shelf life otherwise the consumer may be inclined to
change to a similar product of another brand. In
contrast a similar product with a long shelf life may be
made in larger batches, held as stock for a longer period
30 of time and the period of time that a consumer stores the
product is not of a great concern to the owners of a
particular brand.

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It is an object of the present invention to provide an air bleaching composition that has improved storage properties.

5 SUMMARY OF INVENTION

We have found that some perfume components degrade per se and reduce the activity of bleaching catalysts over a period of time. We have found that by carefully selecting certain perfume components the stability of a bleaching
10 composition, which is substantially devoid of a peroxygen bleach or a peroxy-based or peroxy-generating bleach system, is improved. The present invention is applicable to both granular and liquid formulations. However, the present invention has particular utility in liquid
15 bleaching compositions.

The present invention provides for a bleaching composition that comprises a perfume component that does not substantially reduce the activity of a transition
20 metal catalyst that functions as described herein.

The present invention provides a liquid bleaching composition comprising:

25 A liquid bleaching composition comprising:

(a) an organic substance which forms a complex with a transition metal for bleaching a substrate with atmospheric oxygen, the bleaching composition upon
30 addition to an aqueous medium providing an aqueous bleaching medium substantially devoid of a peroxygen

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bleach or a peroxy-based or peroxy-generating bleach system;

(b) between 0.001 to 3 wt/wt % of a perfume composition; and,

5

(c) the balance carriers and adjunct ingredients to 100 wt/wt % of the total bleaching composition,

wherein the bleaching activity of the beaching
10 composition is greater by a factor of at least 10, in comparison to a same bleaching composition in which a molar equivalent amount of citronellal is present as the perfume composition, after a period of storage at 37 °C for 14 days as measured by exhibited bleaching activity
15 of the transition metal catalyst towards acid blue 45 in the presence of hydrogen peroxide.

Alternatively, beta-carotene may be used as the monitor to measure activity of the catalyst. In instances where
20 the transition metal catalyst exhibits only measurable bleaching activity via air rather than with added peroxy species, in particular hydrogen peroxide, beta-carotene may be used to determine the relative activity of the transition metal catalyst.

25

The factor is at least 12, most preferably 15.

Preferred perfume components may be selected from the group consisting of: Alpha demascone, Delta demascone,
30 Iso E super, Cinnamic aldehyde, Hexylcinnamic aldehyde, Aldehyde butylcinnamic, benzaldehyde, anisique aldehyde, Linalol, Tetrahydrolinalol, Undecavertol, Geraniol,

Nerol, Citronellol, citral, Oxyde de Rose, Geranyl acetate, Citronellyl acetate, Coumarine, Linalyl acetate, Geranyl nitrate, Citronellyl nitrile, Cinnamonnitrile, and Citronitrile, Aldehyde Amylcinnamique,

5 Methylantranilate, di-Ethyl-Anthranilate, Methyl-n-Acetylantranilate, Diphenyloxide, Verdox, Benzylacetate, Diola, Orange Cristals, Peonile, Clonal, Limonene, Camphor, Anthranilate, Di-isobutyl-Anthranilate, Verdyl Acetate, pinane, veloutone, alpha-methylionone, and
10 damascenone.

The term "substantially devoid of a peroxygen bleach or a peroxy-based or peroxy-generating bleach system" should be construed within spirit of the invention. It is
15 preferred that the composition has as low a content of peroxy species present as possible. It is preferred that the bleaching formulation contains less than 1 % wt/wt total concentration of peracid or hydrogen peroxide or source thereof, preferably the bleaching formulation
20 contains less than 0.3 % wt/wt total concentration of peracid or hydrogen peroxide or source thereof, most preferably the bleaching composition is devoid of peracid or hydrogen peroxide or source thereof. In addition, it is preferred that the presence of alkyl hydroperoxides is
25 kept to a minimum in a bleaching composition comprising the ligand or complex of the present invention.

The present invention extends to a method of bleaching a substrate/textile with a composition of the present
30 invention. The method comprising the steps of treating a substrate with the bleaching composition in an aqueous

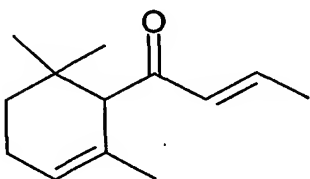
environment, rinsing the substrate and drying the substrate.

The present invention also extends to a commercial
5 package together with instructions for its use.

DETAILED DESCRIPTION OF THE INVENTION

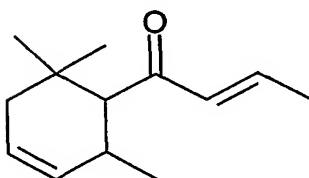
STABLE PERFUMES

10 The following is a list of perfume components that do not unduly effect the stability of an "air" bleaching catalyst in a bleaching formulation.

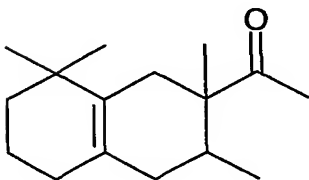


Alpha demascone

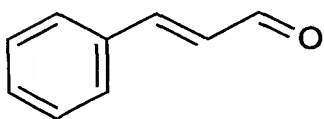
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Delta demascone

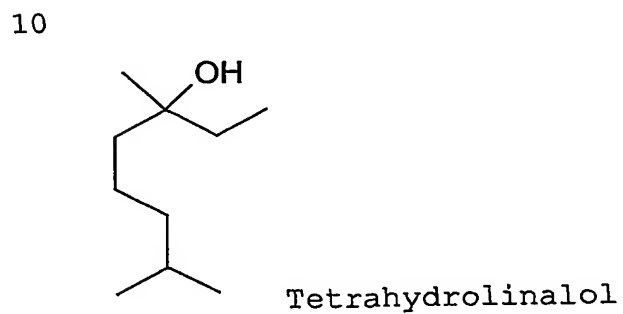
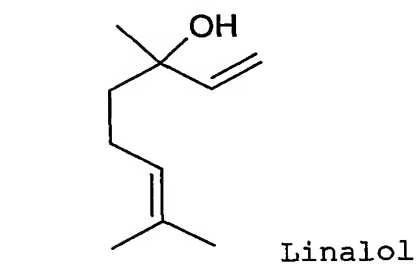
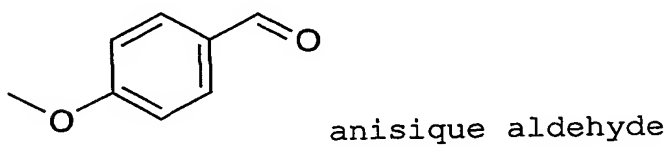
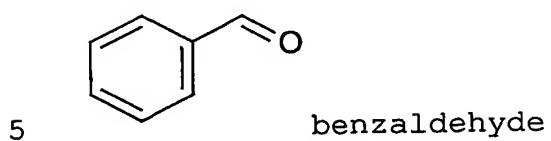
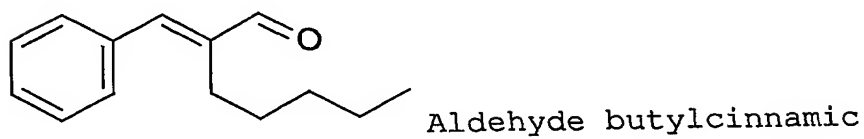
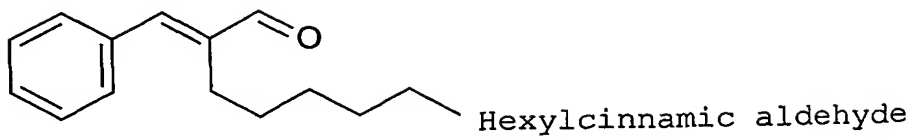


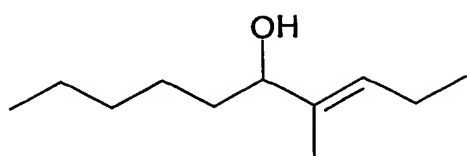
Iso E super



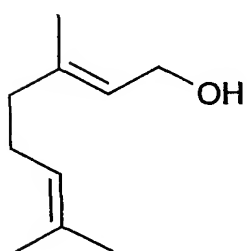
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Cinnamic aldehyde

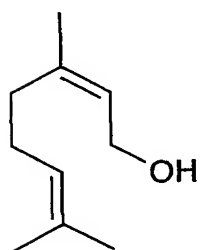




Undecavertol

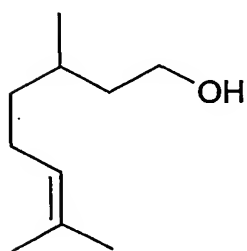


Geraniol

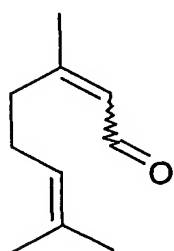


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Nerol

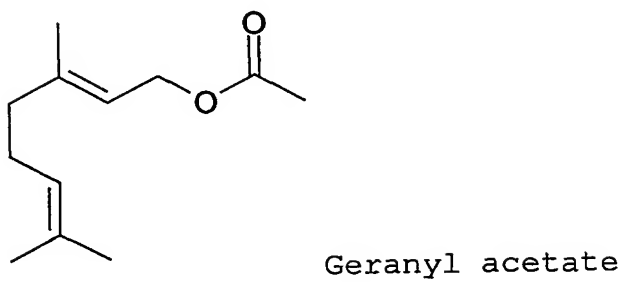
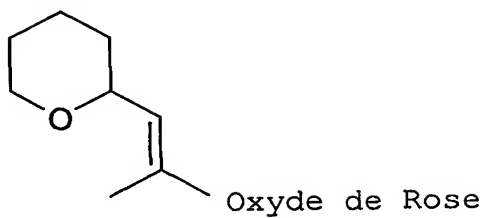


Citronellol

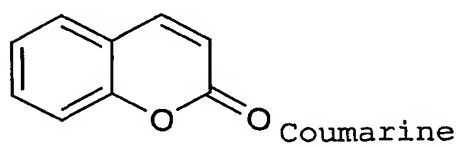
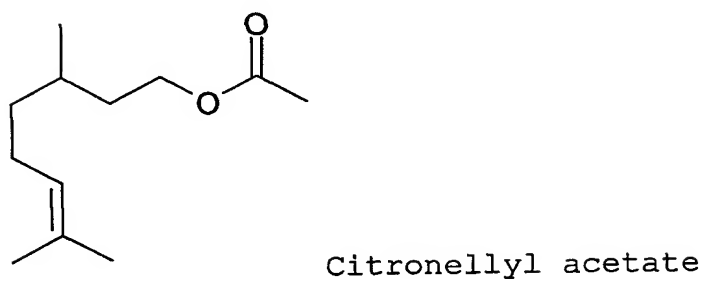


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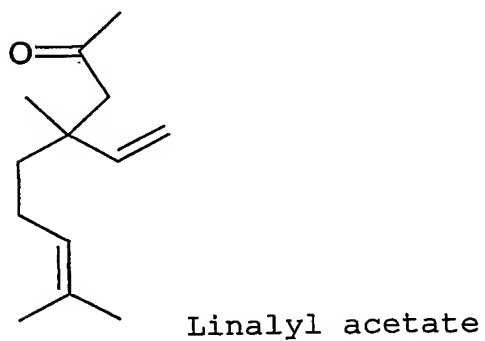
citral

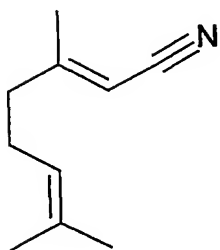


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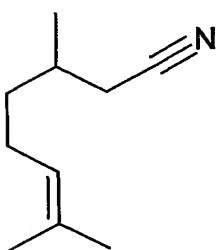


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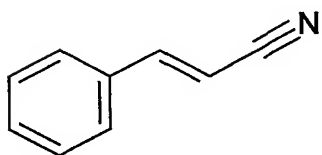


Geranyl nitrile

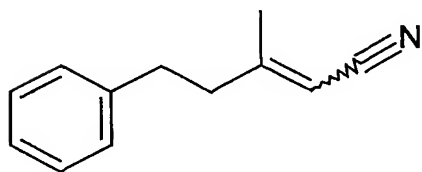


Citronellyl nitrile

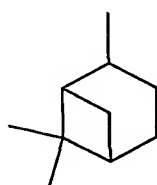
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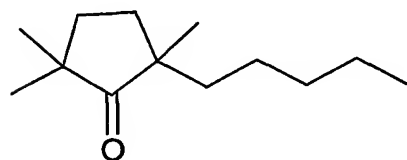
Cinnamonnitrile



Citronitrile

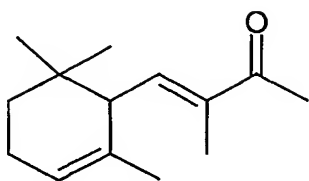


pinane

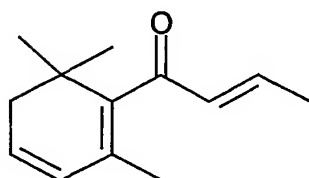


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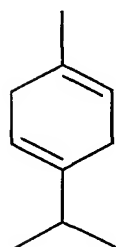
veloutone



Alpha-methylionone



damascenone

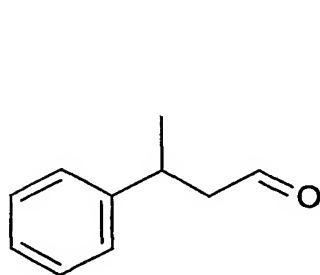


Gamma-terpinene

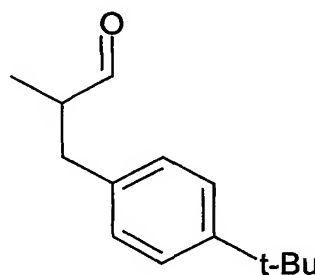
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UNSTABLE PERFUMES

The following is a list of perfume components that unduly effect the stability of an "air" bleaching catalyst in a bleaching formulation.

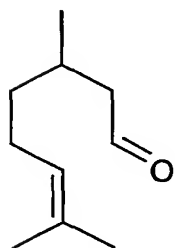


trifernal

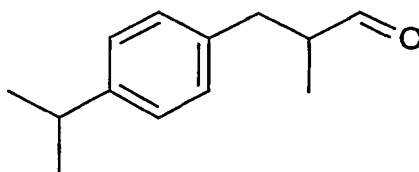


t-Bu lilial

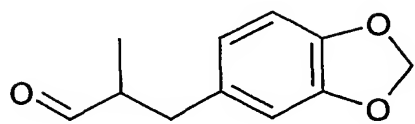
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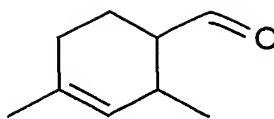
citronellal



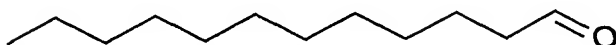
cyclosal



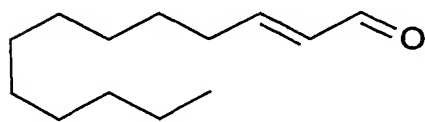
heliopropenal



zestover

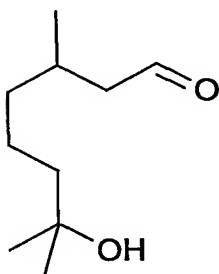


Aldehyde C12

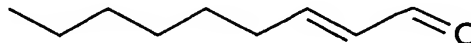


tridecylenal

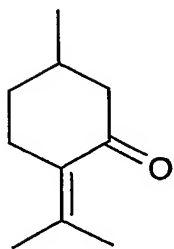
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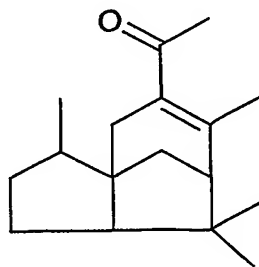
Cyclosia base



octenal

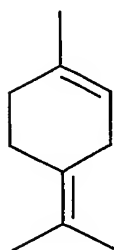


pulegone



vertofix coeur

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terpinolene

THE BLEACH CATALYST

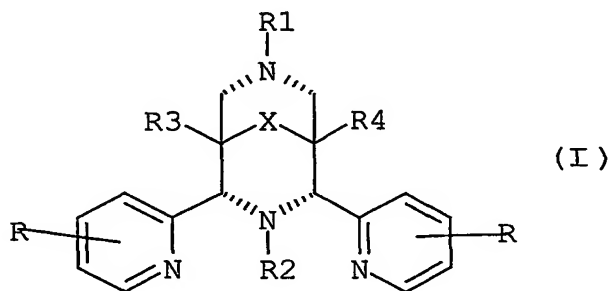
The bleach catalyst per se may be selected from a wide
5 range of transition metal complexes of organic molecules
(ligands). In typical washing compositions the level of
the organic substance is such that the in-use level is
from 0.05 μ M to 50 mM, with preferred in-use levels for
domestic laundry operations falling in the range 1 to 100
10 μ M. Higher levels may be desired and applied in
industrial textile bleaching processes. A mixture of
different catalysts may be employed in the bleaching
composition.

15 Suitable organic molecules (ligands) for forming
complexes and complexes thereof are found, for example
in:
GB 9906474.3; GB 9907714.1; GB 98309168.7, GB
98309169.5; GB 9027415.0 and GB 9907713.3; DE 19755493;
20 EP 999050; WO-A-9534628; EP-A-458379; EP 0909809; United
States Patent 4,728,455; WO-A-98/39098; WO-A-98/39406,
WO 9748787, WO 0029537; WO 0052124, and WO0060045 the
complexes and organic molecule (ligand) precursors of
which are herein incorporated by reference. An example of
25 a preferred catalyst is a transition metal complex of
MeN4Py ligand (N,N-bis(pyridin-2-yl-methyl)-1,1-
bis(pyridin-2-yl)-1-aminoethane).

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The ligand forms a complex with one or more transition metals, in the latter case for example as a dinuclear complex. Suitable transition metals include for example: manganese in oxidation states II-V, iron II-V, copper I-III, cobalt I-III, titanium II-IV, tungsten IV-VI, vanadium II-V and molybdenum II-VI.

An example of a preferred catalyst is a monomer ligand or transition metal catalyst thereof of a ligand having the formula (I):



wherein each R is independently selected from: hydrogen, F, Cl, Br, hydroxyl, C1-C4-alkylo-, -NH-CO-H, -NH-CO-C1-C4-alkyl, -NH₂, -NH-C1-C4-alkyl, and C1-C4-alkyl;

R1 and R2 are independently selected from:

C1-C4-alkyl,

C6-C10-aryl, and,

a group containing a heteroatom capable of coordinating to a transition metal, wherein at least one of R1 and R2 is the group containing the heteroatom;

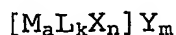
R3 and R4 are independently selected from hydrogen, C1-C8 alkyl, C1-C8-alkyl-O-C1-C8-alkyl, C1-C8-alkyl-O-C6-C10-aryl, C6-C10-aryl, C1-C8-hydroxyalkyl, and -(CH₂)_nC(O)OR₅

wherein R₅ is independently selected from: hydrogen, C1-C4-alkyl, n is from 0 to 4, and mixtures thereof; and,

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X is selected from C=O, $-[C(R_6)_2]_Y-$ wherein Y is from 0 to 3 each R₆ is independently selected from hydrogen, hydroxyl, C1-C4-alkoxy and C1-C4-alkyl.

- 5 The transition metal complex preferably is of the general formula (AI):



10 in which:

M represents a metal selected from Mn(II)-(III)-(IV)-(V), Cu(I)-(II)-(III), Fe (II)-(III)-(IV)-(V), Co(I)-(II)-(III), Ti(II)-(III)-(IV), V(II)-(III)-(IV)-(V), Mo(II)-(III)-(IV)-(V)-(VI) and W(IV)-(V)-(VI),

15 preferably from Fe(II)-(III)-(IV)-(V);

L represents the ligand, preferably N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane, or its protonated or deprotonated analogue;

20 X represents a coordinating species selected from any mono, bi or tri charged anions and any neutral molecules able to coordinate the metal in a mono, bi or tridentate manner;

Y represents any non-coordinated counter ion;

a represents an integer from 1 to 10;

25 k represents an integer from 1 to 10;

n represents zero or an integer from 1 to 10;

m represents zero or an integer from 1 to 20.

BALANCE CARRIERS AND ADJUNCT INGREDIENTS

30 These are generally surfactants, builders, foam agents, anti-foam agents, solvents, and enzymes. The use and amounts of these components are such that the bleaching

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composition performs depending upon economics, environmental factors and use of the bleaching composition.

5 The air bleach catalyst may be used in a detergent composition specifically suited for stain bleaching purposes, and this constitutes a second aspect of the invention. To that extent, the composition comprises a surfactant and optionally other conventional detergent
10 ingredients. The invention in its second aspect provides an enzymatic detergent composition which comprises from 0.1 - 50 % by weight, based on the total detergent composition, of one or more surfactants. This surfactant system may in turn comprise 0 - 95 % by weight of one or
15 more anionic surfactants and 5 to 100 % by weight of one or more nonionic surfactants. The surfactant system may additionally contain amphoteric or zwitterionic detergent compounds, but this is not normally desired owing to their relatively high cost. The enzymatic detergent
20 composition according to the invention will generally be used as a dilution in water of about 0.05 to 2%.

In general, the nonionic and anionic surfactants of the surfactant system may be chosen from the surfactants
25 described "Surface Active Agents" Vol. 1, by Schwartz & Perry, Interscience 1949, Vol. 2 by Schwartz, Perry & Berch, Interscience 1958, in the current edition of "McCutcheon's Emulsifiers and Detergents" published by Manufacturing Confectioners Company or in
30 "Tenside-Taschenbuch", H. Stache, 2nd Edn., Carl Hauser Verlag, 1981.

Suitable nonionic detergent compounds which may be used include, in particular, the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example, aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Specific nonionic detergent compounds are C₆-C₂₂ alkyl phenol-ethylene oxide condensates, generally 5 to 25 EO, i.e. 5 to 25 units of ethylene oxide per molecule, and the condensation products of aliphatic C₈-C₁₈ primary or secondary linear or branched alcohols with ethylene oxide, generally 5 to 40 EO.

Suitable anionic detergent compounds which may be used are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher C₈-C₁₈ alcohols, produced for example from tallow or coconut oil, sodium and potassium alkyl C₉-C₂₀ benzene sulphonates, particularly sodium linear secondary alkyl C₁₀-C₁₅ benzene sulphonates; and sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum. The preferred anionic detergent compounds are sodium C₁₁-C₁₅ alkyl benzene sulphonates and sodium C₁₂-C₁₈ alkyl sulphates. Also applicable are surfactants such as those described in

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EP-A-328 177 (Unilever), which show resistance to salting-out, the alkyl polyglycoside surfactants described in EP-A-070 074, and alkyl monoglycosides.

- 5 Preferred surfactant systems are mixtures of anionic with nonionic detergent active materials, in particular the groups and examples of anionic and nonionic surfactants pointed out in EP-A-346 995 (Unilever). Especially preferred is surfactant system that is a mixture of an
10 alkali metal salt of a C₁₆-C₁₈ primary alcohol sulphate together with a C₁₂-C₁₅ primary alcohol 3-7 EO ethoxylate.

The nonionic detergent is preferably present in amounts greater than 10%, e.g. 25-90% by weight of the surfactant
15 system. Anionic surfactants can be present for example in amounts in the range from about 5% to about 40% by weight of the surfactant system.

One skilled in the art will appreciate that some
20 adventitious peroxy species may be in the composition nevertheless it is most preferred that the bleaching composition of the present invention has less than 1%, preferably less than 0.1%, most preferably less than 0.01%, of a peroxy species present. These adventitious
25 peroxy are predominantly alkyl hydroperoxides formed by autoxidation of the surfactants.

The composition may contain additional enzymes as found in WO 01/00768 A1 page 15, line 25 to page 19, line 29,
30 the contents of which are herein incorporated by reference.

Builders, polymers and other enzymes as optional ingredients may also be present as found in WO0060045.

Suitable detergency builders as optional ingredients may
5 also be present as found in WO0034427.

The composition of the present invention may be used for laundry cleaning, hard surface cleaning (including cleaning of lavatories, kitchen work surfaces, floors,
10 mechanical ware washing etc.). As is generally known in the art, bleaching compositions are also employed in waste-water treatment, pulp bleaching during the manufacture of paper, leather manufacture, dye transfer inhibition, food processing, starch bleaching,
15 sterilisation, whitening in oral hygiene preparations and/or contact lens disinfection.

In the context of the present invention, bleaching should be understood as relating generally to the
20 decolourisation of stains or of other materials attached to or associated with a substrate. However, it is envisaged that the present invention can be applied where a requirement is the removal and/or neutralisation by an oxidative bleaching reaction of malodours or other
25 undesirable components attached to or otherwise associated with a substrate. Furthermore, in the context of the present invention bleaching is to be understood as being restricted to any bleaching mechanism or process that does not require the presence of light or activation
30 by light.

BLEACHING FORMULATION

The present invention has particular utility for liquid formulations because in contrast to a solid heterogeneous mixture in a liquid formulation the contact between
5 individual components are more intimate and hence more susceptible to degradation due to interaction of components.

There are many commercial liquid formulations for
10 detergents and rinse conditioners or other liquid products that may be enhanced by conferring a bleaching ability to the liquid formulation. As will be evident to one skilled in the art the present invention is applicable to known liquid formulations and liquid
15 formulations to be developed.

The level of the catalyst in a commercial bleaching composition is from 0.0001 to 0.6 wt/wt %, preferably 0.001 to 0.15 wt/wt %, most preferably 0.01 to 0.1 wt/wt
20 %. We have found that the level of catalyst is optimum between 0.03 to 0.09 wt/wt % in the commercial bleaching composition.

The present invention extends to both isotropic and
25 complex liquid compositions and formulations a brief discussion of which follows. Some isotropic formulations are termed 'micro-emulsion' liquids that are clear and thermodynamically stable over a specified temperature range. The 'micro-emulsion' formulation may be water in
30 oil, or oil in water emulsions. Some liquid formulations are macro-emulsions that are not clear and isotropic. Emulsions are considered meta-stable. Concentrated, clear

compositions containing fabric softening actives have been disclosed in WO 98/08924 and WO 98/4799, both Procter & Gamble. Such compositions comprise bio-degradable fabric conditioners. However, both disclose compositions comprising water miscible solvents that do not form water-in-oil micro-emulsions. Clear fabric conditioning compositions have also been disclosed in EP 730023 (Colgate Palmolive), WO 96/19552 (Colgate Palmolive), WO 96/33800 (Witco Co.), WO 97/03170 (Procter & Gamble), WO 97/03172 (Procter & Gamble), WO 97/03169 (Procter & Gamble), US 5492636 (Quest Int.) and US 5427697 (Procter & Gamble). Liquid formulations of the present invention may contain for example; monoethoxy quats; AQAs and bis-AQAs; cationic amides; cationic esters; amino/diamino quats; glucamide; amine oxides; ethoxylated polyethyleneimines; enhancement polymers of the form linear amine based polymers, e.g. bis-hexamethylenetriamine; polyamines e.g. TETA, TEPA or PEI polymers.

The liquid may be contained within a sachet as found in WO02/068577.

The following is an example of a liquid bleaching composition to which an organic substance which forms a complex with a transition metal for bleaching a substrate with atmospheric oxygen may be added together with the selected stable perfume components.

Ingredient	Wt%
Nonionic surfactant	26.6
Monopropylene glycol	5.5
Pigment premix	0.017
Glycerol	21.36
Monoethanolamine	7.56
Oleic fatty acid	13.10
Water	Up to 100
Linear alkyl benzene sulfonate	20.1
Perfume	1.6
Protease Enzyme	1.0

The following are further examples of commercial liquid
5 formulations that the present invention may be
incorporated into: Wisk™ liquid USA, 1999, OMO™ liquid
NL, 1999, OMO-liquido™ Brazil, 1999, and Rinse
conditioner (Robijn™ - NL). In this regard, that
catalyst is added together with the selected stable
10 perfume components.

The following is a further example of a commercial liquid
formulation that the present invention may be
incorporated into by adding the catalyst together with
15 the selected stable perfume components. The commercial
liquid formulation has a pH of 7.

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Sodium citrate:	3.2 %
Polypropylene glycol:	4.75 %
LAS-acid:	5.6 %
NI 25 9 EO:	6.6 %
LES (anionic sufactant):	10.5 %
Borax:	2.30 %
Sorbitol:	3.35 %
Alcosperce 725:	0.30 %
Coconut fatty acid:	0. 73 %
Monoethanolamine:	0.20 %
Fluorescer:	0.125 %
Enzymes	-
Perfume/dye	-

It is most preferred that when the catalyst is in a
5 liquid composition, the liquid composition has a pH of 7
or below irrespective.

The following catalyst was used in the experiments 9,9-
dihydroxy-2,4-di-(2-pyridyl)-3-methyl-7-(pyridin-2-
10 ylmethyl)-3,7-diaza-bicyclo[3.3.1]nonane-1,5-
dicarboxylate Iron (II) dichloride was prepared as
described by Heidi Borzel, Peter Comba, Karl S.
Hagen, Yaroslaw D. Lampeka, Achim Lienke, Gerald Linti,
Michael Merz, Hans Pritzkow, Lyudmyla V. Tsymbal in
15 Inorganica Chimica Acta 337 (2002) 407 - 419. WO0248301
provides synthetic details of similar compounds.

Liquid compositions containing 0.03 % wt/wt of a bleach
component and 0.06 % wt/wt of individual perfume

components are stored in glass vials for 14 days at 37 °C in a cabinet.

The activities were determined at 40 °C in a H₂O₂

- 5 containing NaH₂PO₄.H₂O pH7 buffer and Acid Blue 45 (CAS No. 2861-02-1) as substrate using the following protocol.

Samples of 70 mg liquid were diluted in 10.00 ml MilliQ water. We added 45 µl of this solution to an assay of 230
10 µL containing 20 mM H₂O₂, 75 µM Acid blue 45 and 54 mM NaH₂PO₄.H₂O pH7 buffer.

The solutions were mixed and pre incubated for 1 min at 40 °C. The changes in absorbance at 600 nm were measured
15 for 8 min at 40 °C using a spectrophotometer.

The absolute changes in absorbance were correlated to activities obtained with freshly prepared calibration samples. The measured activities were expressed as µMol/l/.

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Table 1: The residual activity of 0.03 % wt/wt of a transition metal catalyst after 2 weeks storage at 37 °C.

Nr	Perfume component (0.06%)	Residual Activity (µMol/l)
1	No addition	1.77
2	Alpha demascone	1.64
3	Delta demascone	1.56
4	Iso E super	1.73
5	Cinnamic aldehyde	1.76
6	Hexylcinnamic aldehyde	1.73
7	Aldehyde butylcinnamic	1.60

8	Benzalaldehyde	1.76
9	Anisique aldehyde	1.70
10	Linalol	1.66
11	Tetrahydrolinalol	1.96
12	Undecavertol	1.76
13	Geraniol	1.73
14	Nerol	1.73
15	Citronellol	1.66
16	Citral	1.63
17	Oxyde de Rose	1.79
19	Geranyl acetate	1.83
20	Citronellyl acetate	1.60
21	Coumarine	1.79
22	Linalyl acetate	1.70
23	Geranyl nitrate	1.76
24	Citronellyl nitrile	1.53
25	Cinnamonnitrile	1.79
26	Citronitrile	1.83
27	Aldehyde Amylcinnamique	1.80
29	Methylantranilate	1.70
30	di-Ethyl-Anthranilate	1.86
31	Methyl-n-Acetylanthranilate	1.73
33	Diphenyloxyde	1.89
34	Verdox	1.79
35	Benzylacetate	1.79
36	Diola	1.86
37	Orange Cristals	1.73
38	Peonile	1.79
39	Clonal	1.70
40	Limonene	1.76
41	Camphor	1.60

42	Anthranilate	1.83
43	Di-isobutylanthranilate	1.60
44	Verdylacetate	1.64
45	Trifernal	0.26
46	Lilial	0.22
47	Citronellal	0.09
48	Cyclosal	0.26
49	Heliopropanal	0.45
50	Zestover	0.55
51	Aldehyde C12	0.45
52	Tridecylenicaldehyde	0.65
53	Cyclosia base	0.52
54	Octenal	0.81
55	Pulegone	0.32
56	Vertofix coeur	0.65
57	Veloutone	1.40
58	Alpha-methylionene	1.14
59	Demascenone	1.01
60	Terpinolene	0.62
61	Gamma-Terpinene	0.98
62	Pinane	1.30